Fabrication of silicon nanostructures with a scanning tunneling microscope

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A technique is presented for fabricating Si nanostructures with a scanning tunneling microscope operated in air. The process involves the direct chemical modification of a H-passivated Si(100) surface and a subsequent liquid etch. The chemically modified portions of the surface can withstand a deep (> 100 nm) liquid etch of the unmodified regions with no etch degradation of the modified surface. At a write speed of 1–10 μm/s, large-area (50 μm $\times$ 50 μm) patterns with lateral feature sizes $\sim$25 nm are reliably fabricated.

The potential for atomic-level manipulation of matter with the scanning tunneling microscope (STM) has spurred significant interest in the use of the STM as a nanofabrication tool.[1] This ultimate limit of manipulation was recently realized with the controlled positioning of single adsorbate atoms on a metallic surface.[2] Although this result is an excellent demonstration of the level of control attainable with a STM, the ability to manipulate single adsorbate atoms on a surface is far removed from practical STM-based device fabrication. A significant obstacle in the process of STM nanostructure fabrication has been the transfer of a written pattern into a usable metallic or semiconductor structure. The problem arises from the fact that the STM is useful in modifying very thin layers of material which by their very nature are not sufficiently robust to withstand the process of actual pattern transfer. Therefore, finding a suitable "resist" for effective pattern transfer is a significant problem.

One potentially attractive technique, which has recently been investigated by Dagata *et al.*, involves the direct chemical modification of a semiconductor surface.[3] In this process a H-passivated Si (111) surface is selectively oxidized with a STM. The process has two advantages. First, the chemical modification involves only the top one or two monolayers of material. Thus, extremely high lateral resolution is feasible. Such fine resolution has recently been demonstrated in ultrahigh vacuum with the selected removal of the passivation from as few as 10 atomic sites.[4] Second, such a modified surface is potentially useful as a mask for subsequent etching or material growth.[5] Although the preliminary etching results were crude, they suggest that direct chemical modification of the Si surface has the potential for successful nanometer-scale device fabrication.

In this letter we demonstrate the realization of this potential by presenting a simple and reliable method for fabricating Si nanostructures with a STM. This fabrication process involves the direct chemical modification of the Si (100) surface with a STM and a subsequent liquid etch of the patterns. The modified surface layer, although only a few monolayers in thickness, is sufficient to withstand a deep (> 100 nm) liquid etch of the unmodified portions of the sample. Large-area (50 μm $\times$ 50 μm) patterns with lateral features size $\sim$25 nm are reliably fabricated with a typical write speed of $\sim$10 μm/s. This constitutes an important step toward the goal of using the STM in the practical fabrication of nanometer-scale device structures.

The mechanism for the STM chemical modification of the H-passivated Si (111) surface was investigated by Dagata *et al.*[3] The chemical passivation of the (111) surface leaves a monohydride-terminated surface which is resistant to oxidation.[6] Exposure to the STM results in local oxidation of this surface. Preliminary results indicate that this oxide provides some level of resistance to liquid etching.[5] However, the properties of the Si(111) surface make effective pattern transfer via liquid etching difficult. This difficulty arises because most etch solutions which do not attack silicon oxide or etch it very slowly also etch the (111) surface relatively slowly.[7] Consequently, etch selectivity, which is important to pattern transfer, is reduced.

An alternative choice for effective pattern transfer is the Si (100) surface. These same solutions etch the Si (100) surface at a much higher rate than the (111) surface.[7] The ⟨100⟩ surface can also be passivated with an oxide-resistant H termination, although the passivation terminates the surface with a dihydride layer which is more susceptible to hydrocarbon contamination.[8] Our results indicate that the STM modifies the passivated (100) surface in a similar manner to the (111) surface without any extraordinary efforts to protect the surface from contamination. In addition, we find that the chemically modified (100) surface is an effective mask to liquid etching, which facilitates pattern transfer into the Si.

The STM lithography was performed on 0.01 Ω cm (100) *n*-type silicon. Each sample was passivated with a 60 s dip in 10% aqueous HF solution and then blown dry. The Si wafers were taken directly from the manufacturers packaging and received no additional cleaning prior to passivation. The samples were mechanically clipped to the sample stage. It should be noted that the use of a conducting paste to attach the samples resulted in irreproducible results which we attribute to surface contamination from the solvents in the paste.

The patterns were written by direct chemical modification of the Si surface with the STM.[3] The STM was operated in air and both dc- and ac-etched tungsten tips

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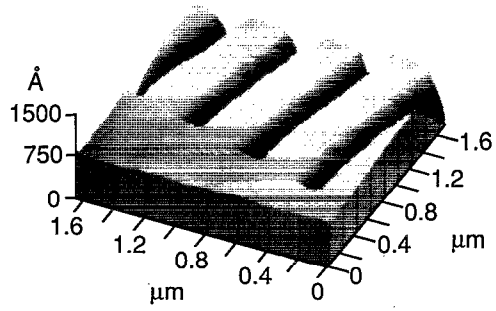

FIG. 1. 1.6 μm$\times$1.6 μm AFM image of a pattern fabricated by direct chemical modification of the H-passivated Si (100) surface and a subsequent etch in hydrazine. The total etch depth is 120 nm.

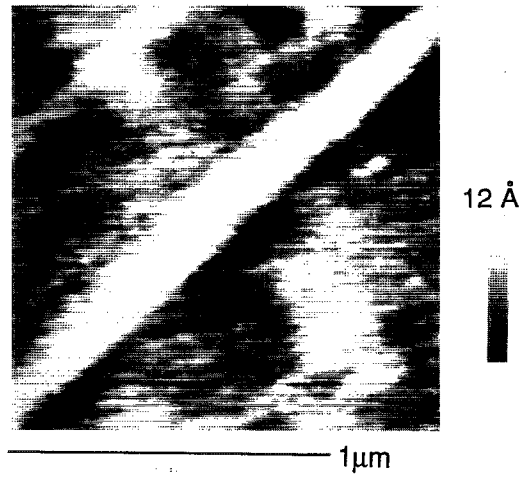

FIG. 2. 1.3 μm$\times$1.3 μm AFM image of a latent pattern generated by direct chemical modification of the H-passivated Si (100) surface. The black-to-white vertical greyscale is 1.2 nm. Note that the pattern height is less than 1 nm.

were used. A piezoelectric scanner with a 125 μm x-y scan range was used to produce patterns large enough to be located with an optical microscope. All patterns were written with a negative tip bias relative to the sample. The patterns were written by applying a dc bias to the tip and scanning the tip over the surface of the sample while under tunneling feedback control which maintained a current of 0.2 nA. After exposure with the STM the samples were liquid etched at room temperature in hydrazine. A 60 °C, 11 molar KOH solution was also used as an etch although the STM-written patterns were prone to degradation after deep etches in KOH. This degradation during deep etches does not occur with hydrazine; although the KOH produces a much smoother etched surface. [*Warning:* Extreme caution should be exercised when using hydrazine since it is highly toxic and potentially explosive.]

An atomic force microscope (AFM) was used to determine the etch depth and the linewidth of the resulting patterns. Figure 1 shows an AFM image of a structure which was fabricated using STM surface modification followed by a hydrazine etch. The pattern was written with a 4 V bias and a write speed of 10 μm/s. The raised areas of the structure correspond to regions of the Si surface exposed by the STM tip. Several features of the structure are notable. First, the unexposed regions of the sample were etched to a depth of 120 nm.[9] Second, the exposed regions of the sample remain unaffected by the etch: the route mean square roughness of the exposed STM-modified surface after etching is 1.7 nm, which is comparable to an unetched modified surface. These two results taken together demonstrate the extreme resistance of the STM-modified surface to the liquid etching process. Therefore, the STM-modified surface is an effective mask for replicating patterns directly into silicon.

This STM surface modification affects only the top few monolayers of the passivated (100) surface. Figure 2 shows a greyscale AFM image of a STM-modified (100) Si surface which has not been etched. The STM was operated at a 4 V tip bias and a write speed of 10 μm/s (the same exposure conditions as in Fig. 1). The diagonal line across the center of the picture is the latent image of a line which was repeatedly scanned by the STM. A second line, parallel to the first, in the upper left corner was generated by a single pass at the same tip voltage and write speed. The AFM measurements of the topography indicate that the change in height of the modified (100) surface is quite small. Even in the case of the repeatedly scanned line the STM modification results in a raised ridge <1 nm high on the surface. Latent images of patterns written at 2 V could not be located with the AFM, while at 1 V the tip creates a slight (<1 nm) indentation in the surface. Such indentations may result fromthe tip scratching the surface under low tunnel bias conditions. It is evident from these AFM images that the STM modifies only the top few monolayers of the surface. This result is consistent with Dagata *et al.*, who also estimate the thickness of the modified layer to be one or two monolayers.[5]

Dagata *et al.* found that the amount of oxygen incorporation in the Si surface was a function of both tip bias and dose.[3] We find that effective etch masks for hydrazine can be written at almost any tip voltage provided sufficient dose is given. Selective exposure, i.e., conditions under which the STM does not write a mask, is successful at low tip voltage (1.5 V) using the KOH etch. Exposure at higher voltages always generates an etch-resistant surface mask although at fast write speeds (>10 μm/s) incomplete exposure occurs, which leads to the etch attacking portions of the exposed regions. Our most reproducible patterns are produced at voltages between 3 and 4 V with a write speed of 1–10 μm/s.

Although the actual surface modification involves only a few monolayers, Fig. 1 clearly demonstrates the effectiveness of this surface layer as an etch mask. The etch solutions we use do not etch Si oxide or etch it very slowly. As in the case of the (111) surface, we believe that the STM locally oxidizes the passivated (100) surface, although we have no way of analyzing the composition of the exposed layer. At this point, we cannot exclude the possibility that surface contamination (perhaps in the form of hydrocarbons) plays a role in the surface modification process, since the (100) surface is particularly susceptible to such con-

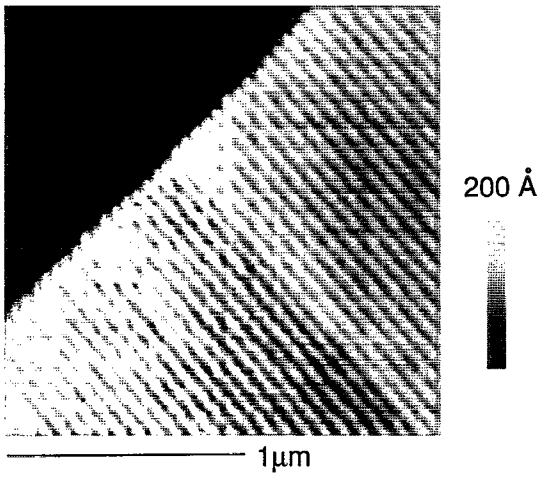

FIG. 3. 1.7 μm$\times$1.7 μm AFM image of a 50 nm pitch grating fabricated in Si by STM patterning and KOH etching. The lines in the lower left section were exposed at 3.5 V, in the upper right 4 V. The width of the 3.5 V lines are $\sim$25 nm and the etch depth is $\sim$15 nm.

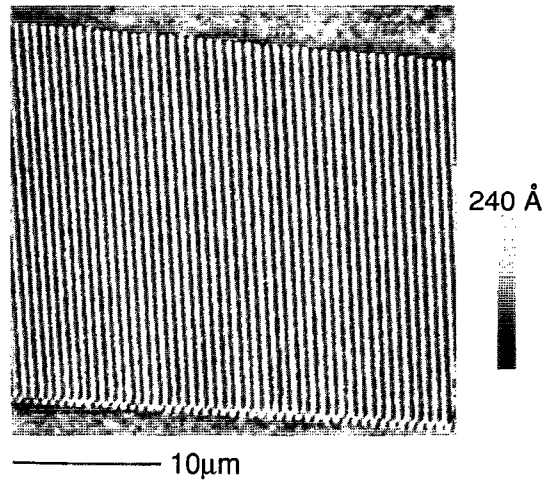

FIG. 4. 30 μm$\times$30 μm AFM image of a large STM-fabricated grating. The grating has a 500 nm period and covers an area 60 μm$\times$25 μm.

tamination. In any case, the process is a reliable method of nanostructure fabrication in silicon, and the exact nature of the surface modification remains a topic for future investigation.

Sub-100 nm etched features are easily and reliably generated by the exposure and etch process. Figure 3 shows an AFM image of a 50 nm period grating written at 3.5 and 4 V. AFM line scans indicate that the lines are $\sim$25 nm FWHM for the 3.5 V exposure. One advantage of STM-based lithography over conventional high energy e-beam lithography is the lack of proximity effects. The exposure dose at a particular point on the surface is independent of neighboring lithography. The fine pitched grating in Fig. 3 was written without any consideration of proximity corrections. Consequently, closely packed features are much easier to produce with STM lithography than with conventional e-beam lithography.

We are therefore able to generate reproducibly etched lines $\sim$25-nm wide in silicon. Our present linewidth is at least partially controlled by the STM tip diameter. This conclusion is based on the fact that blunt tips (as viewed optically) typically yield larger linewidths than sharp tips, and that a tip crash usually increases the minimum feature size. We expect that even finer feature sizes can be reliably fabricated. This expectation is supported by the fact that STM modification of the hydrogen-passivated (111) Si surface in ultrahigh vacuum indicates that as few as 10 surface sites can be removed selectively.[4] Therefore, further optimization of such relevant parameters such as the passivated surface conditions, the ambient atmosphere during exposure, and the tip size, and tunneling conditions should decrease the minimum attainable feature size.

In addition to small feature size, it is also possible to fabricate uniform features over large areas. Figure 4 shows a 30 μm$\times$30 μm AFM image of a portion of a 500 nm period etched grating (full size: 60 μm$\times$25 μm). The grating was written at 4 V with a write speed of 10 μm/s and etched in KOH. Note the uniformity of the lines and the relative smoothness of the etched regions. Figure 4 clearly demonstrates that relatively large-area uniform structures are easily fabricated with this STM lithography.

In conclusion, we have shown that STM surface modification of the Si (100) surface and subsequent liquid etching is an effective means of fabricating sub-100 nm features. Since the surface modification involves only the top few monolayers of the Si surface, we expect that sub-10 nm size features are feasible. The process is reliable and can be done in air without great care to protect the surface from contamination.

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[9] Figure 1 shows an apparent etch depth less than the value quoted in the text. This is because the low aspect ratio of the AFM tip would not allow it to reach the bottom between the lines. The actual etch depth was measured at an edge of the pattern.